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Computational and Experimental tools for the Characterization of Catalysts for Proton-Exchange-Membrane Fuel Cells

Thesis defense

by

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Presentation Outline

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- Introduction
  - Basics of Fuel Cells
  - Catalysts used in PEM
  - Oxygen Reduction Reaction in Cathode
- Computational Simulation
  - Computational Method
  - Results
  - Summary
- Microscopy Characterization
  - Introduction
  - Experimental setup
  - Results and Discussions
- Conclusion and Future Work
- Acknowledgement

Introduction

Fuel cell

- An electrical cell that converts the intrinsic chemical free energy of a fuel directly into direct-current electrical energy in a continuous catalytic process. Fuel cell technology is based upon the simple combustion reaction.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

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Basic reactions in PEM fuel cell

- At anode:

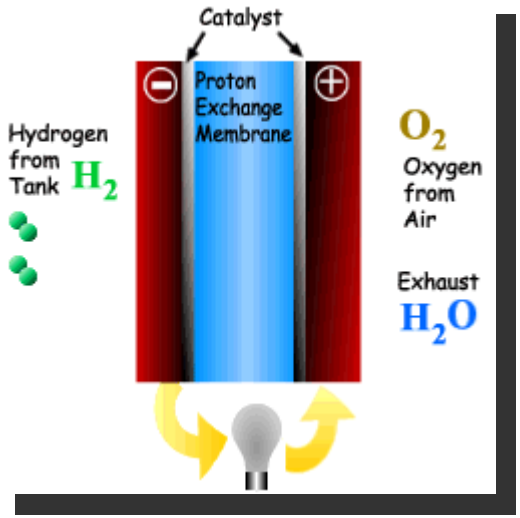
$2H_2 \rightarrow 4H^+ + 4e^-$

- At cathode:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_20$

- Overall reaction:

$2H_2 + O_2 \rightarrow 2H_2O$ + energy



Catalyst used in PEM

- As PEM fuel cell operates at low temperature, electrocatalysts are necessary to perform H_2 and O_2 reduction.
- Pt is used widely as they are very stable and has high activity.
- Problems associated with the use of platinum
  - oxygen reduction reactions (ORR) on Pt are much slower compared with hydrogen oxidation reactions on Pt surfaces
  - Aspects related to Pt cost and reserves
  - Aspects related to Pt supply

Non Noble Metal Catalyst

- N4-metal macrocycles have been of interest in this respect.
- Heat treatment of Fe- or Co-N_4 macrocycles improves
  - the activity,
  - their stability
- Increasing order of activity Cu ~ Ni < Co < Fe.
- The interaction essential for the catalysis takes place between the oxygen and the central metal ion.

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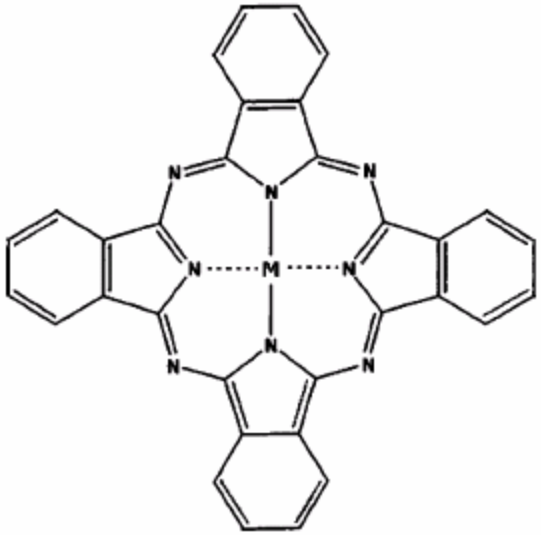
Phthalocyanines

- It is of great interest because of
  - Low material cost
  - High thermal stability
  - Good chemical resistance



Oxygen Reduction Reaction

- Oxygen reduction in an acid medium may occur according to the following reactions:
  - $O_2 + 4\,H^+ + 4e^- \longrightarrow 2H_2O \quad E1^o = 1.23\ V$
  - $O_2 + 2\,H^+ + 2e^- \longrightarrow H_2O_2 \quad E2^o = 0.68\ V$
  - $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \quad E3^o = 1.77\ V$

  (chemical reaction)

ORR

- Reduction directly through 4e- transfer

or

Two 2e- transfer with H_2O_2 as intermediate

- 4e- reduction has a higher catalytic activity as it has higher Potential.

ORR

- Essential interaction takes place between the oxygen and the central metal ion.
- The adsorption of dioxygen is the first step for ORR.
- The interaction of oxygen molecule and its effect on dissociation of O-O bond is important to understand the reaction mechanism.
- Hence different models have been proposed for the dioxygen interaction with the metal.

- Molecular modeling is a useful tool to understand these mechanisms and to obtain a method to screen catalysts which enhances one of these pathways.
- It reduces cost, time and gives flexibility to create different solvent effects, and calculate the thermodynamic properties without any discrepancies.

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Molecular Modeling

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Computational Method

- In this study Materials Studio DMOL3 (version 4.1) was employed.
- Density functional theory (DFT) calculations were carried out with VWN-BP functional.
- DFT semicore pseudopotential was applied
- DNP (double numerical plus) polarization function basis sets are employed for all the calculations.
- The vertical ionization potentials are calculated sing SCF method.

The following Phthalocyanines were investigated using DNP basis set

- Iron Phthalocyanine FePc
- Iron tetrasulfophthalocyanine FeTsPc
- Cobalt Phthalocyanine CoPc.

MOLECULAR MODELING

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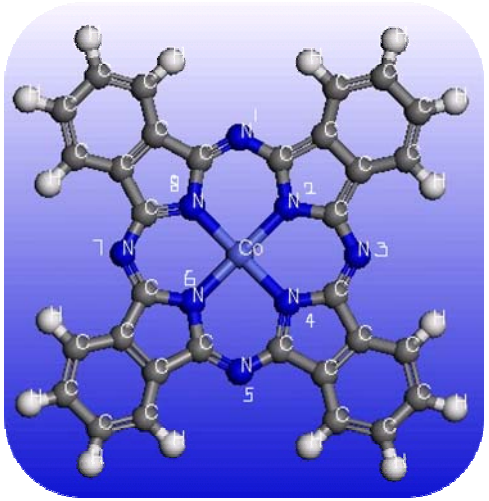
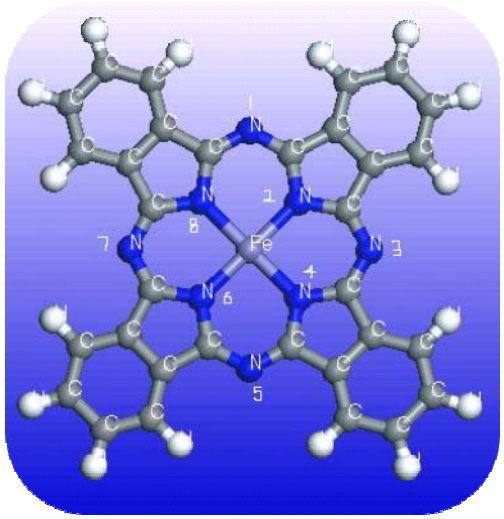
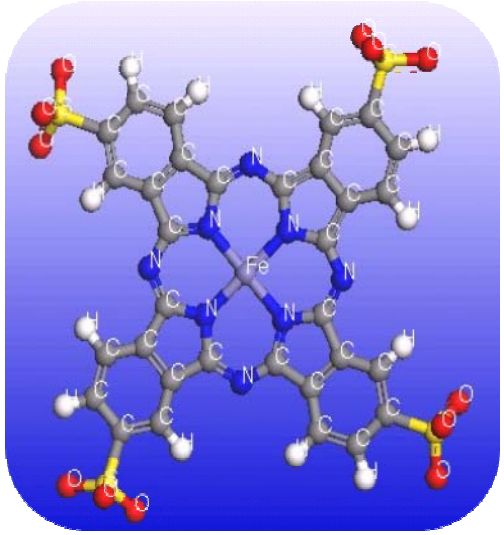
Cobalt Phthalocyanine



Iron Phthalocyanine



Iron tetrasulfophthalocyanine



Results of distance between Metal and Nitrogen

	This work- Aº	Experimental result * Aº	Other work ** Aº
CoPc	1.927	1.91	1.92
FePc	1.93	1.928	1.923
FeTsPc	1.93	-	1.923

* X-ray diffraction results

** DFT study of Transitional Metal Macrocyclic Complexes – National Research Council Institute of Fuel Cell Innovation

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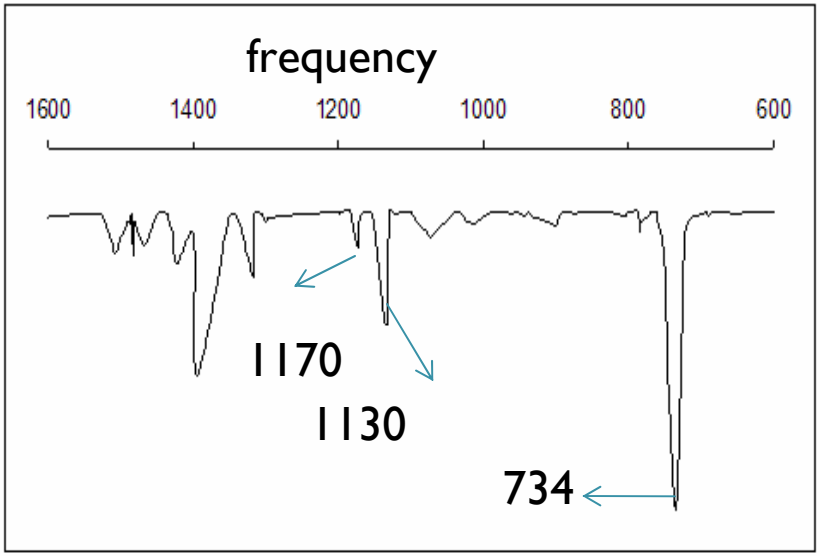
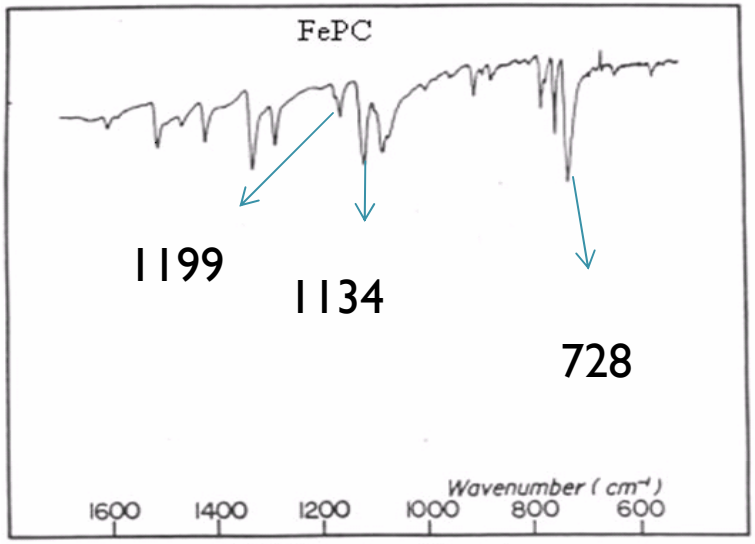
FePc Frequency Results

Simulation Results



Experimental Results



A quantatively good agreement is achieved. The characteristic ring breathing peak at 734cm-1, Fe-Pc at 958 cm-1 (994cm-1 experimental), 1130cm-1 and 1170 cm-1 {1134cm-1(C-H bending) and 1199cm-1 from experiment}.

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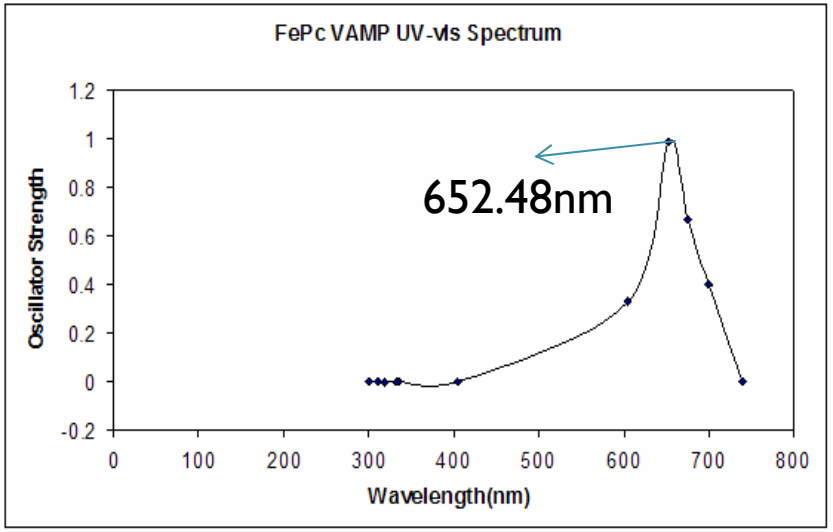
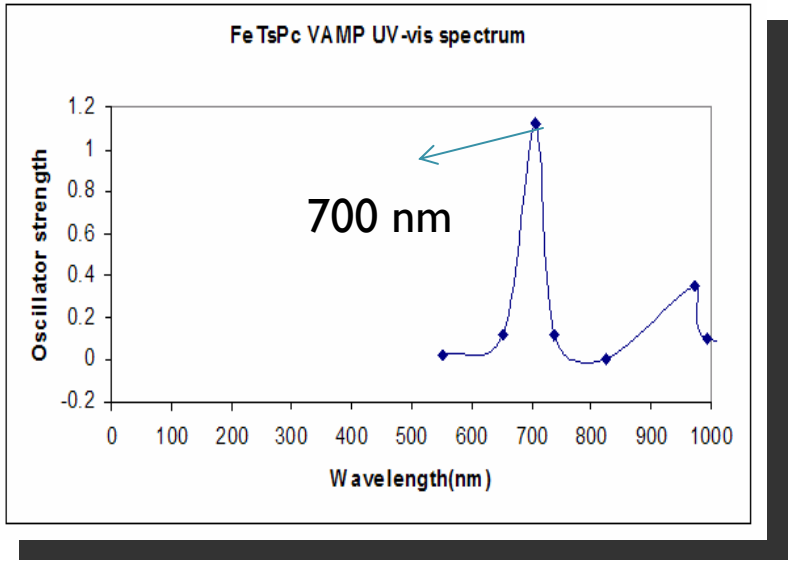
UV vis spectrum

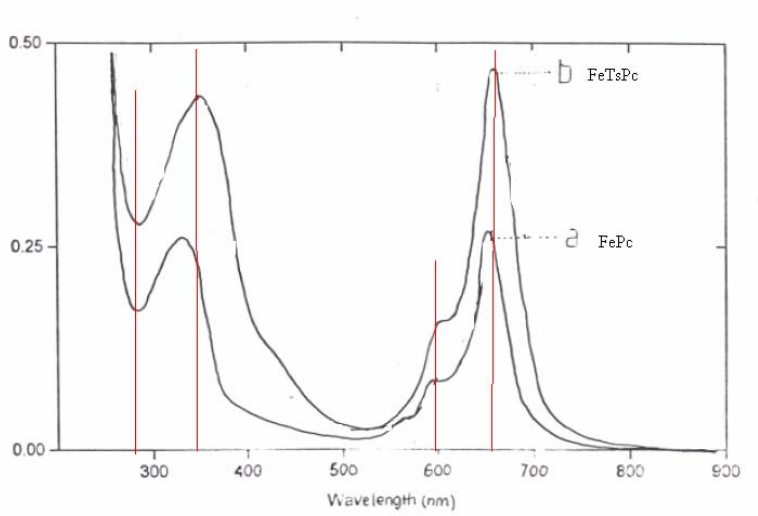
- FePC UV vis spectrum
- FeTspc uv vis spectrum





Experimental results

- By comparing with the experimental UV-vis adsorption spectra for FePc and FeTsPc, qualitatively good agreements are achieved



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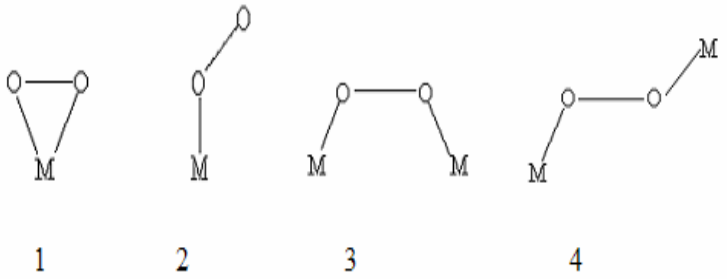
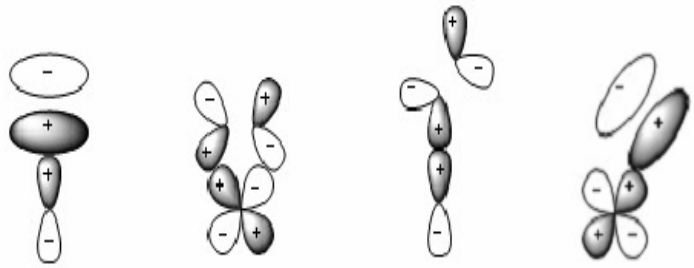
Models of the reaction pathways

- Griffiths (1) and Pauling models (2)
- Molecular orbitals involved in different interactions of O_2 with a metal center
- The most probable structure for O_2 adsorptions is Pauling model i.e. adsorption through single O and metal atoms





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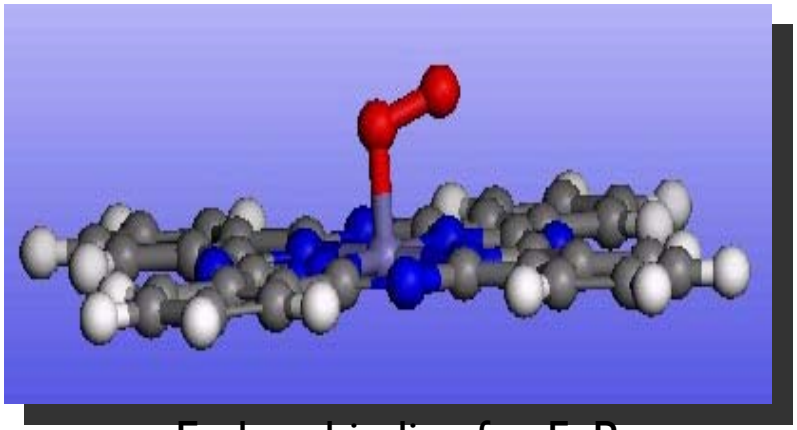
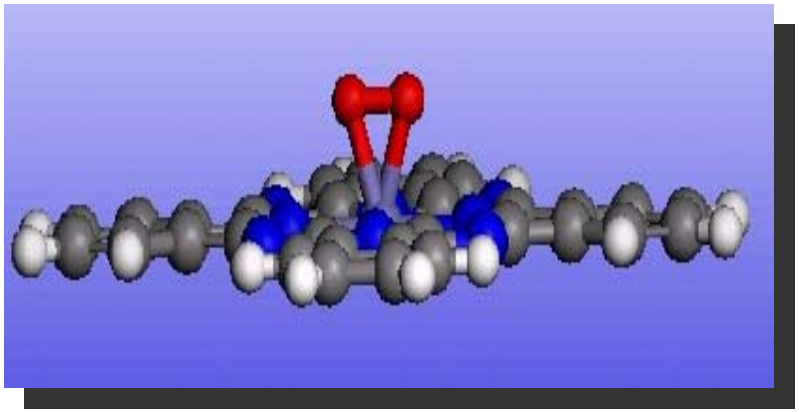
Oxygen Adducts of Pthalocyanines



End on binding for FePc



Side on binding for FePc

As shown above the end on and side on oxygen bonding properties are calculated for CoPc, FePc, and FeTsPc and the results are compared with the experimental results.

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Calculated Dioxygen abducts properties (this work) for end on and side on reactions

	R_{O-O}	R_{M-O}	E_{bO2} End on eV	E_{bO2} Side on eV
CoPc	1.184	1.940	-0.399	1.91
FePc	1.279	1.761	-0.72	1.64
FeTsPc	1.274	1.764	-0.69	1.7

$$E_{bO2} = E_{ML-O2} - (E_{O2} + E_{ML})$$

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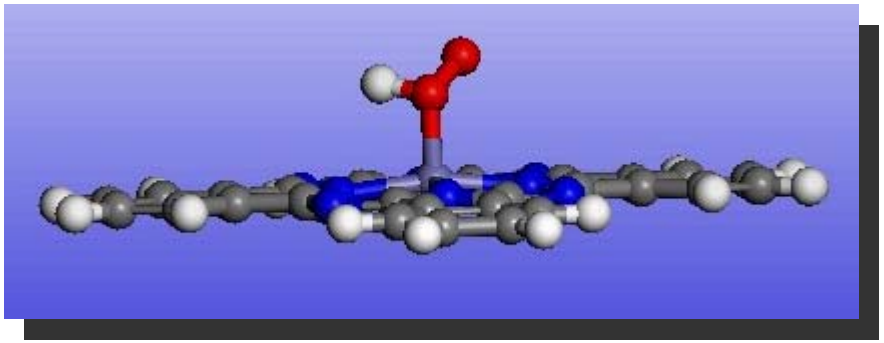
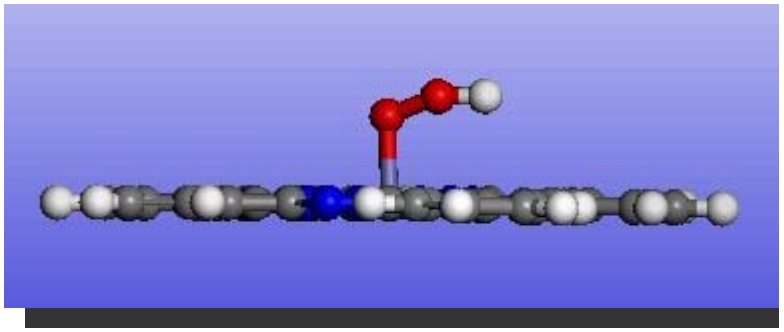
- Hydrogen Dissociation energies





As shown above the hydrogen bonding properties are calculated for CoPc, FePc, and are compared with the experimental results

	Hydrogen bonded to Oxygen Farther away from Metal	Hydrogen bonded to the oxygen closer to the metal
CoPc	-1.3	-2.2
FePc	-0.2	-1.6

$$E_{bO2} = E_{ML\text{-}O2\text{-}H} - (E_{O2} + E_{ML} + E_H)$$

Hydrogen reaction pathways also depends on the central metal.

- In CoPc, Hydrogen bonding to the oxygen farther away from the metal is favorable.
- In FePc, Hydrogen bonding to the oxygen closer to the metal is more stable.

Summary

- Dioxygen-binding abilities of the transition metal macrocyclic complexes are determined by central metal.
- End-on reactions are more favorable than the side-on reactions.
- FePc is more stable than the CoPc in the end-on reaction .
- Larger dioxygen-binding energy are associated with better catalytic activity.
- Activity trend observed for phthalocyanine systems can be rationalized with oxygen-binding ability.
- For phthalocyanine systems, iron derivatives have good ionization potential and large oxygen-binding energy.

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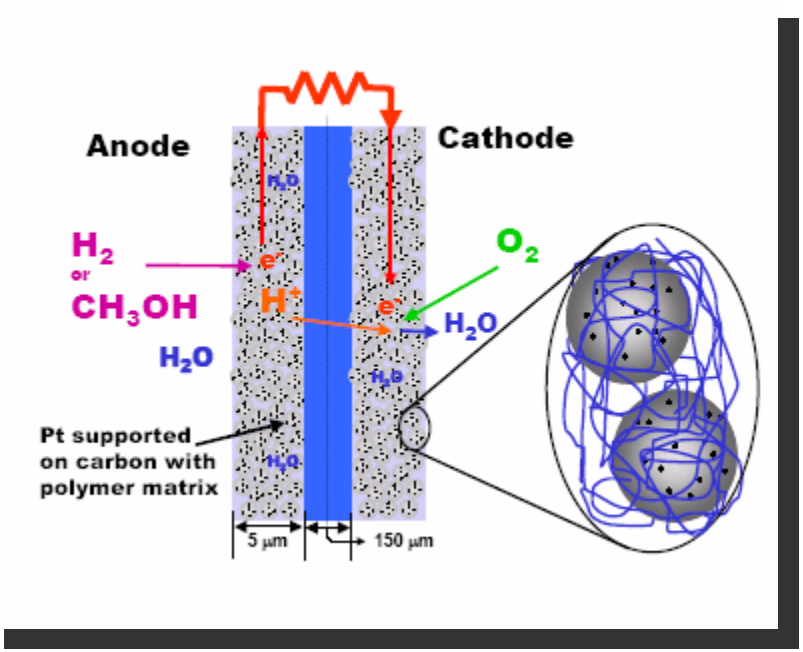
Microscopy Characterization

Microscopy characterization

- Microscopy Characterization – to develop novel catalyst.
- Approximate durability of the membrane
- In-situ experiments
- Calculate thermodynamic properties

MEA - Contains TWO electrodes with Platinum catalyst bonded to the PEM

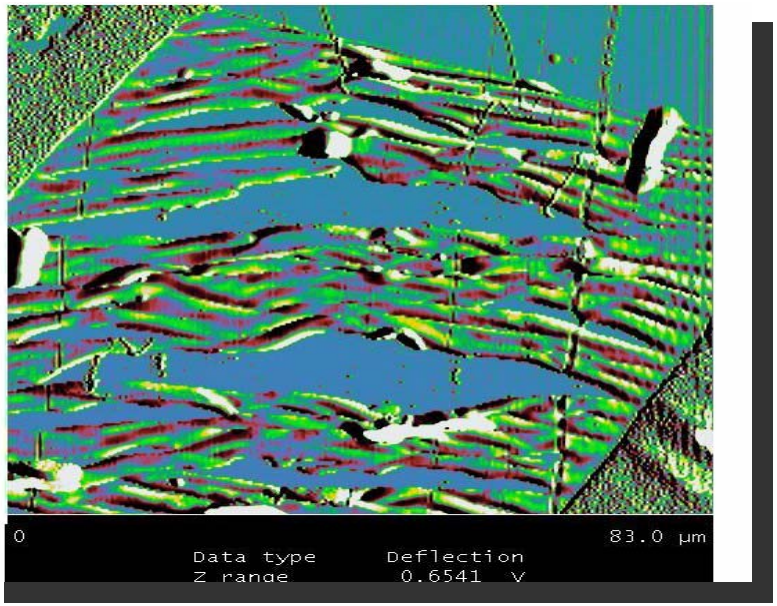


Morphology by AFM

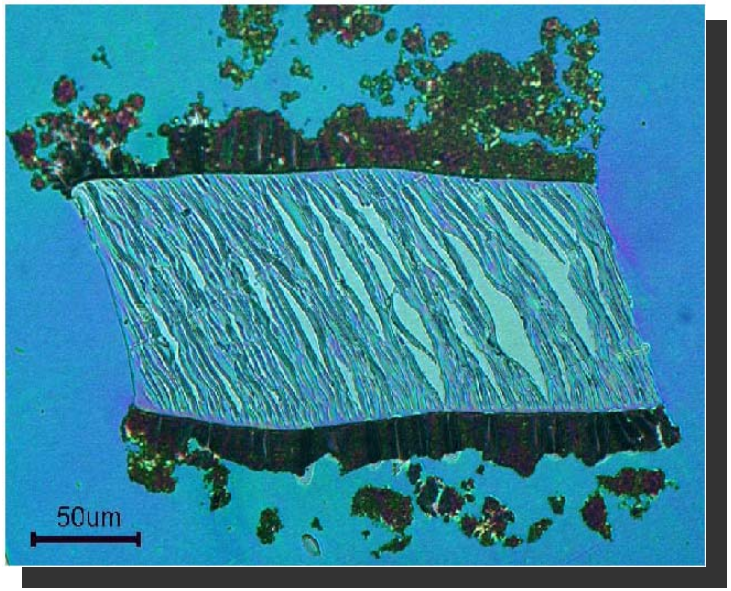
- AFM – better for polymer characterization.
- provides access to much smaller structures than optical microscopy while simultaneously allowing quantitative measurements of objects in all three dimensions.
- Polymer materials, which are too sensitive to an electron beam to be studied with SEM or TEM, can be easily investigated with AFM
- In addition to imaging, AFM (Atomic Force Microscopy) applications include studies of mechanical, adhesive and electromagnetic forces

Validation

- cross section of Membrane observed by AFM



- Cross section of Membrane observed by TEM



Cross-section of Electrode: The structure of the cross section of the membrane (Nafion is the middle region and the ink (electrode) on both the sides) is observed by AFM and is agreed with the Transmission Electron Microscopy (TEM) results

Experimental setup

- The samples were mounted on magnetic stainless steel sample stubs
- The size of the probe is selected and accordingly the force module is changed in AFM setup.
- Laser is set for maximum deflection.
- The samples were imaged using contact mode.
- Height mode is used to observe the 3D image while the deflection image provides better topography features of the sample surfaces.

Ink Preparation

The samples are prepared as described below:

- Select the catalyst (platinum/Ruthenium)
- Add 0.8 ml of Nafion 115c and 0.7 ml of ethanol to appropriate amount of catalyst.
- Mix them in an ultrasonic homogenizer until they form a homogenous mixture.
- A thin layer of this ink is coated on HOPG (Highly ordered pyrolytic Graphite) and is dried under the hot gun at low temperature.

Two Methods of adding ink(electrode) on the membrane:

- In the first method-
  - painted directly onto the membrane
  - dried to form the condensed catalyst layer or electrode.
  - This method requires that the ink solution does not dissolve the membrane during painting, or otherwise compromise its integrity during the painting process.
- In the second Method-
  - two-step method- first painted and dried onto a decal or "blank" the size of the desired active area.
  - The painted and dried decal is then hot-pressed against the membrane at temperatures of typically 150-200°C and pressures of 3000 psi, to bond the composite in the electrode to the membrane.

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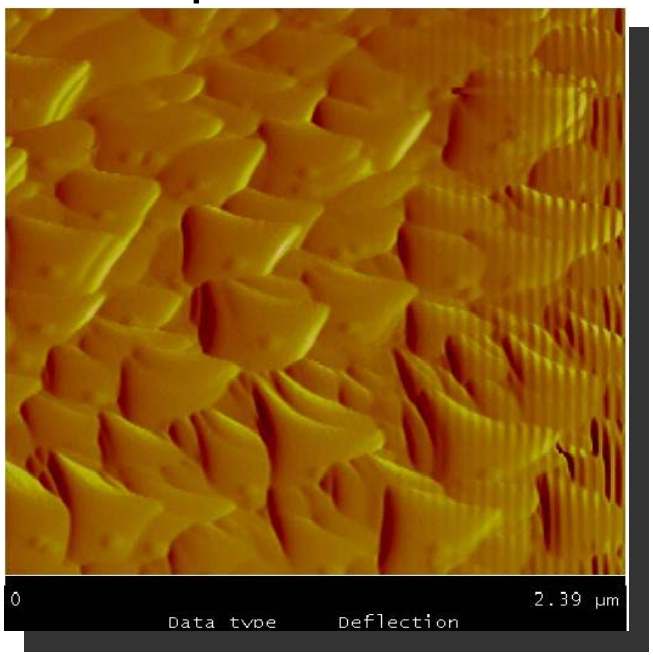
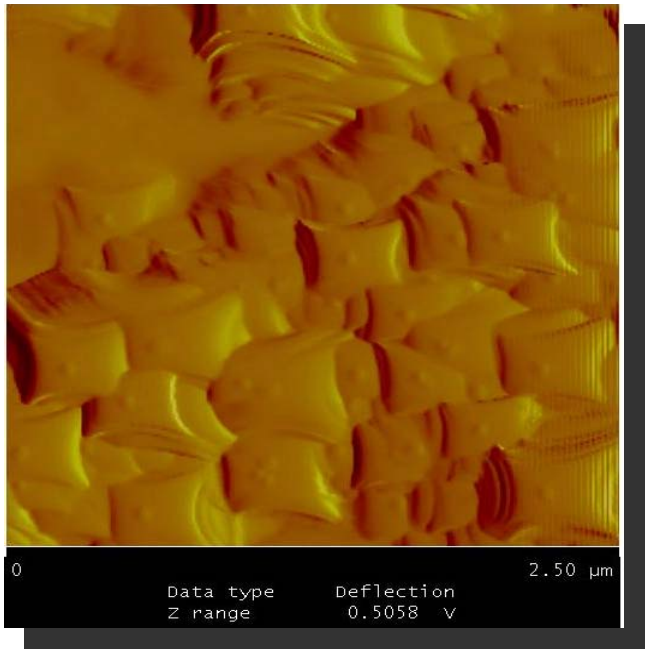
Results

- structure of the electrode in the sample*



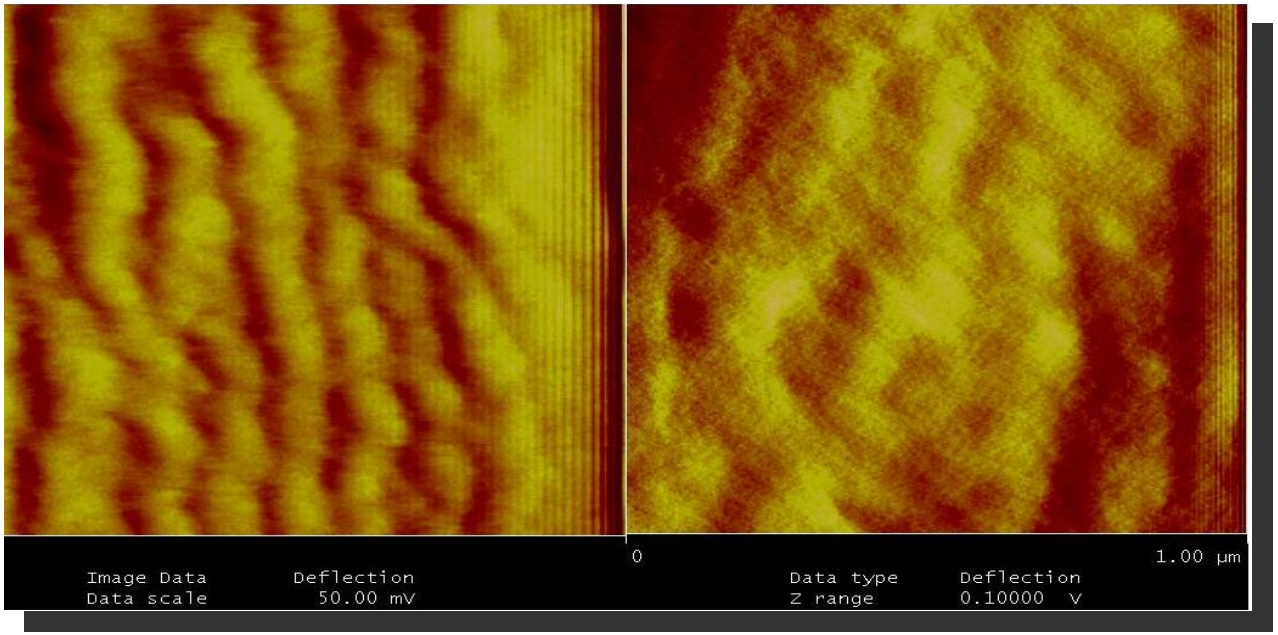
- Structure of the electrode prepared in LAB



Structure of Pt and Carbon Particles: an image of Pt particles on carbon particles were observed for the cross-section sample before the fuel cell operation. Similar AFM image was also observed for the sample prepared in our lab.

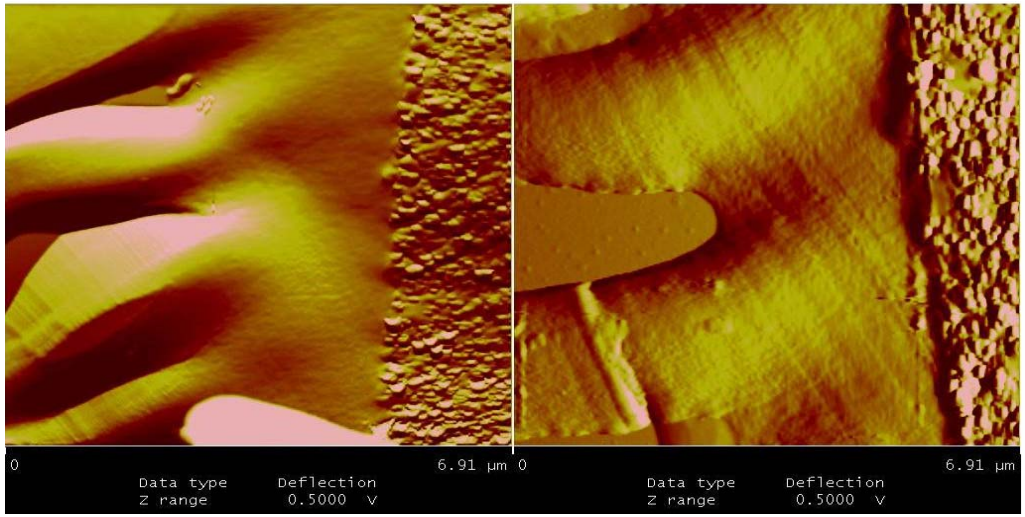
MICROSCOPY CHARACTERIZATION

Comparison of the Cross section of MEA before and after Fuel cell Operation



Structure of Nafion Membrane: The images of cross section of MEA before and after fuel cell operation were obtained and revealed the zig-zag structures of the Nafion membrane

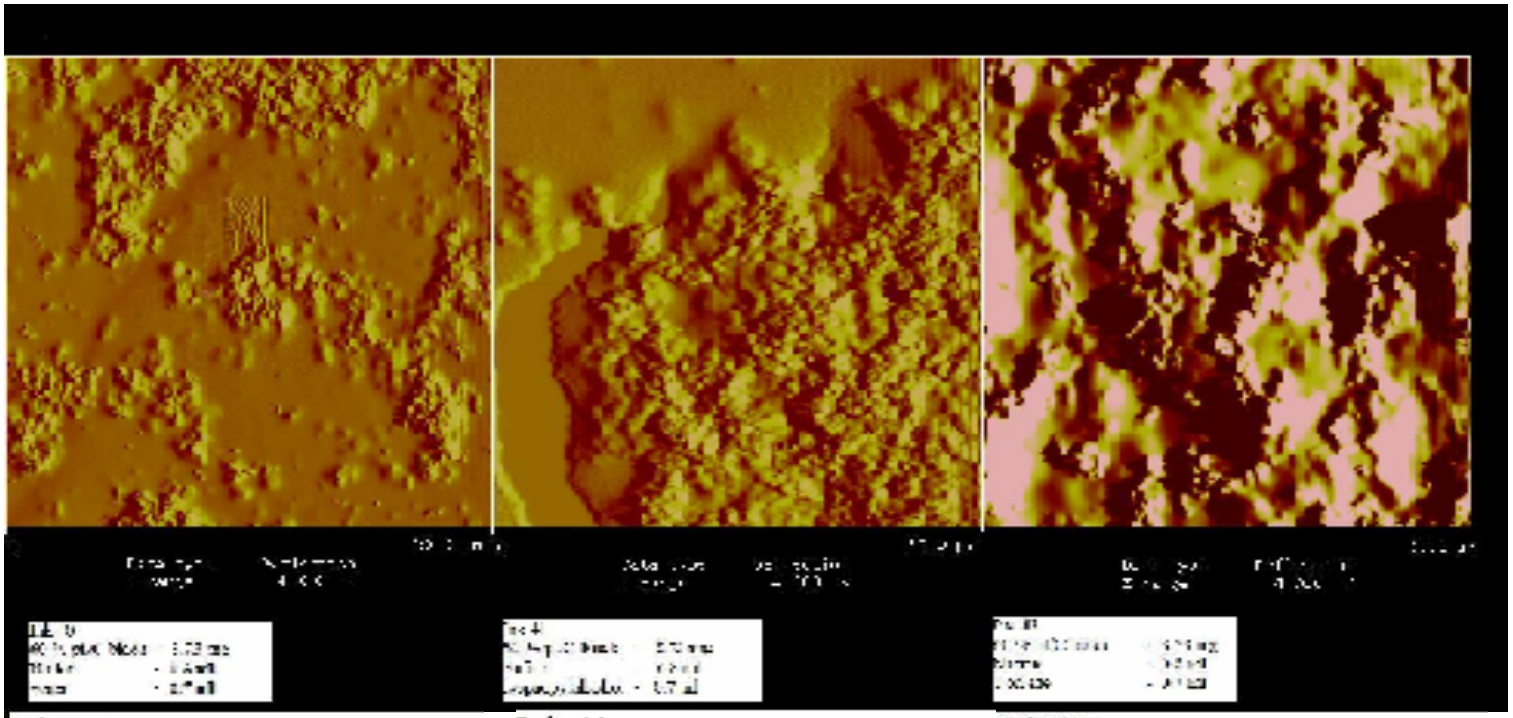
Comparison of Interface degradation before and after fuel cell operation



The interface degradation between the catalytic layer and Nafion membrane were observed after the fuel cell operation

MICROSCOPY CHARACTERIZATION

Comparison of different Inks



Ink 40		Ink 41		Ink 43	
60 % pt/C black	- 8.73 mg	60 % pt/C black	- 8.73 mg	60 % pt/C black	- 8.73 mg
Nafion	- 0.8 ml	Nafion	- 0.8 ml	Nafion	- 0.8 ml
water	- 0.7 ml	Isopropylalcohol	- 0.7 ml	Toluene	- 0.7 ml

MICROSCOPY CHARACTERIZATION

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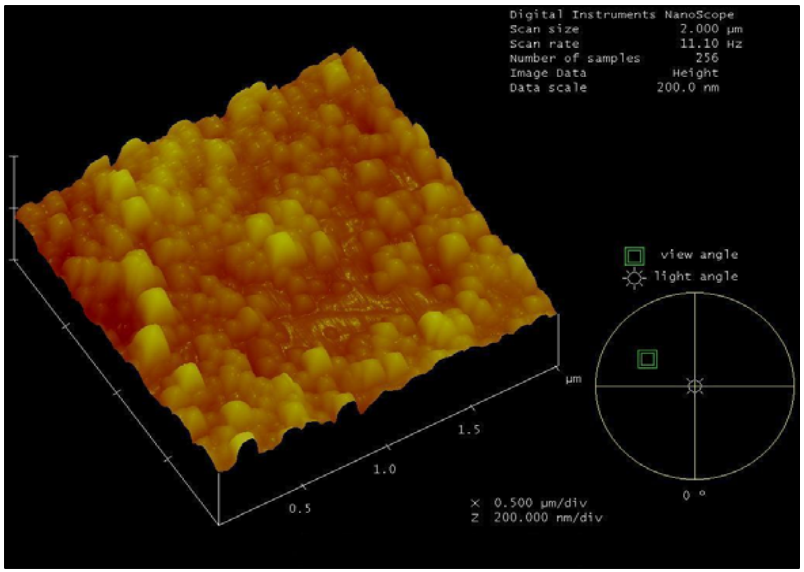
3D Structure of carbon particles



Summary

- AFM is a useful tool to study the structures of membrane and catalysts for PEM fuel cell.
- Method of preparation of electrode is reliable and the fundamental understandings using our small electrode will be applicable to the commercial products

CONCLUSION

- Validation of the use of DMol3 and the application of Density Functional theory to screen non noble metals for their catalytic activity
- Intermediate reaction mechanism for Iron and Cobalt phthalocyanines are simulated.
- It is observed that the End-on reactions are more favourable than the side-on reactions.
- FePc is more stable than the CoPc in the end-on reaction Mechanism proving it to be a better catalyst for Oxygen Reduction Reaction. Hydrogen bonding also depends on the central metal.
- Atomic Force Microscopy is indeed a better tool to look at the morphology as it gives the flexibility to run the in situ experiments thus simulating the actual environment of the fuel cell.
- Method of Ink (electrode) preparation is validated.
- It also provides us with the 3 D images for the catalysts which can be useful to look at the Z direction (height) of the particles.

Future Work

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- Simulate crystal structures for their catalytic activity.
- Create solvent affects to observe the change in the catalytic activity in different solvents.
- Further investigate the morphology as a function of operating conditions such as time, temperature, humidity etc.
- Obtain the Experimental results for Oxygen reduction for different materials through electrochemical tests.

Thus by using AFM, molecular modeling and electrochemical tests, we have a better understanding of reaction mechanisms of Oxygen reduction at cathode in PEM fuel cells and would help develop a novel catalyst which will have better durability and efficiency.

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THANK YOU !

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QUESTIONS